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THE ACID HYDROLYSIS OF  
ETHYL DICHLOROACETATE IN  
ACETONE-WATER SOLVENT

by

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INTRODUCTION

Even though it is possible to make qualitative predictions about the influence of substitution on the various factors involved in solvent effect for reactions in solution, there has been, as yet, few attempts to unravel the quantitative aspects of the problem with a view to building up a comprehensive theory of solvent influence on reaction velocities. In this connection an investigation of the rates of hydrolysis of substituted halogen esters in mixed solvents was expected to be very valuable. The results of a study of the acid catalyzed and neutral hydrolysis of ethyl dichloroacetate are reported in this communication.

EXPERIMENTAL

Purification of Materials

Acetone: Acetone was purified as reported before (Ref. Tech. Rep. No. 6 Nr 057-233).

Ethyl dichloroacetate: The ester was shaken up with 3% sodium bicarbonate solution to remove free acid, washed with distilled water, dried over anhydrous  $\text{CaSO}_4$  for three days and distilled under reduced pressure. The fraction

boiling between 131 and 131.5° C. under 401 mm pressure was collected for use.

All water used was double distilled, a little potassium permanganate being added before the second distillation.

Procedure:

Stock solutions of  $\text{Ba}(\text{OH})_2$  and HCl of strengths 0.0250 N and 0.6000 N respectively were prepared from analytical reagent grade materials and these were standardized using potassium acid phthalate, phenolphthalein serving as indicator. The strengths of the stock solutions were checked periodically.

All glassware used was standardized. The thermostats employed controlled temperature within  $\pm 0.02^\circ \text{C}$ . at  $25^\circ \text{C}$ . and  $35^\circ \text{C}$ . and within  $\pm 0.03^\circ \text{C}$ . at  $65^\circ \text{C}$ .

The procedure for preparing solutions for kinetic runs was the same as reported in previous studies on ester hydrolysis. The required volume of acetone, kept at the temperature of the experiment, was pipetted into a 100 ml volumetric flask, the required amount of the standard acid to make a 0.0500 N solution was added and the contents made up approximately to the neck of the flask with water. The solution was then left in the bath for 1½ to 2 hours to attain temperature equilibrium. Each run was started by adding the required volume of the ester from a micropipette to make a 0.0500 N solution and making up with water at the temperature of the bath. The flask was withdrawn, well shaken and quickly returned to the bath.

The time of shaking was taken as starting time since in most cases the ester does not go into solution until it is shaken. 10 ml. samples were withdrawn at convenient intervals and run into crushed ice prepared from the purified water and titrated against Standard Calcium Hydroxide (approximately 0.025 N, actual standardization was to four significant figures) using bromophenolblue as indicator.

The procedure for neutral hydrolysis was the same except no acid was added to the run.

The unimolecular rate constants  $k'$  for the acid catalyzed and  $K_n$  for neutral runs were obtained from plots of  $\log (a-x)$  against  $t$ . Where  $(a-x)$  is the concentration of unreacted ester at time  $t$ . The true rate constant  $k_a$  for the acid catalyzed reaction was calculated from the expression

$$k' = k_a (H) + k_n$$

Activation energies in the case of acid hydrolyses were calculated from plots of  $\log k$  vs  $\frac{1}{T}$ . Since neutral hydrolysis was done at two temperatures only, the values were calculated straight from the velocity constants.

The low solubility of  $\text{Cl}_2\text{CHCOOEt}$  in water-rich solvent mixtures limited the range of investigation. An ester concentration of 0.05 M was desirable for reasonable accuracy in the measurements by the procedure employed and it is impossible to prepare a solution of that strength even in 40% acetone. The solvent compositions employed in the study were 50, 60, 70, and 80% by volume of acetone.

The specific reaction rate constants were in general reproducible to within  $\pm$  3-5%. The greatest variation (5%) was found in the solutions containing the larger percentages of acetone.

### Discussion

The velocity constants for both acid and neutral hydrolysis in the various media are given in Tables I and II. The plots (Figs. I and II) indicating the change of the rate constant with solvent composition are roughly of the same shape as obtained by Nair and Anantakrishnan (1).

Table I

(Acid hydrolysis,  $k$  in liters mole $^{-1}$  hour $^{-1}$ )

Temp.	25° C	35° C	45° C	
Vol. % of Acetone	Dielectric Constant	Dielectric Constant	Dielectric Constant	
50	52.0 <sub>9</sub>	8.27	49.7 <sub>9</sub>	16.10
60	45.5 <sub>9</sub>	6.28	43.4 <sub>9</sub>	12.05
70	39.6 <sub>0</sub>	3.95	37.7 <sub>8</sub>	8.02
80	32.1 <sub>0</sub>	2.62	30.5 <sub>6</sub>	6.35

Table II

(Neutral Hydrolysis,  $k$  in liters mole $^{-1}$  hour $^{-1}$ )

Temp.	35° C.		45° C.	
	Vol. % of Acetone	Dielectric Constant	Dielectric Constant	Dielectric Constant
50	49.7 <sub>9</sub>	17.5 <sub>6</sub>	47.8 <sub>7</sub>	37.04
60	43.4 <sub>9</sub>	7.01	41.8 <sub>0</sub>	15.61
70	37.7 <sub>8</sub>	2.27	35.5 <sub>5</sub>	5.47
80	30.5 <sub>6</sub>	0.885?	29.2 <sub>5</sub>	1.60

and Hockersmith and Amis (2) for acid hydrolysis of ethyl acetate and methyl propionate respectively in acetone-water systems. The activation energies and frequency factors for acid catalyzed and neutral hydrolysis are shown in Tables III and IV.

Table III  
Acid Hydrolysis

% Acetone	$\log_{10}$ PZ	E in cals.
50	8.59	13,200
60	8.68	13,500
70	8.71	13,800
80	9.68	15,300

Table IV  
Neutral Hydrolysis

% Acetone	$\log_{10}$ PZ	E in cals.
50	7.53	14,500
60	7.91	15,600
70	8.49	17,100
80	4.10 ?	11,500 ?

The changes in activation energy and PZ factor are in the expected direction for halogen substitution at the  $\alpha$  position. The decrease in activation energy is more than compensated by the decrease in the PZ factor and hence the hydrolysis is very slow compared to that of ethyl acetate.

The specific velocity constant for the neutral hydrolysis in 80 percent acetone solvent at the lower

temperature ( $35^{\circ}$  C) seems to be in error. This is because of the extremely small value of the constant at this high acetone concentration and at this lower temperature. The activation energies and PZ values which result from calculations using this value of the rate constant are consequently in error and have therefore been neglected in this discussion. The questionable values of these quantities have, however, been inserted in Tables II and IV.

In order to compare the effect of variation of dielectric constant on reaction rate for the substituted ester with that for unsubstituted ester a plot of  $\log \frac{k}{C_{H_2}O}$  against  $\frac{1}{D}$  was made. The division by  $C_{H_2}O$ , the concentration of water in solution, takes care of the molecularity with respect to water. The plots indicate linear variation of  $\log k$  with  $\frac{1}{D}$  within the range 50-75% acetone. A sharp upward curvature somewhere around 25% acetone is indicated. The interesting feature about these curves is that they have a negative slope for the straight line portion while those for ethyl acetate show a positive slope. Decrease of dielectric constant here result in decrease of  $k/C_{H_2}O$ . The change in slope can be readily explained as follows.

If the field of the  $\alpha$ -chlorine atoms, which have acquired partial negative character, is assumed to be the determining factor in the approach of the water molecule to the reaction center, then the negative slopes of the plots are readily understood. The association of the solvent molecules involved at the group in question

will be closer as the dielectric constant of the medium is decreased. Change in the extent or nature of solvation of the strongly polar  $-\text{CHCl}_2$  group may also be partly responsible for the observed trend. This can result in a lessening of the inductive withdrawal of electrons from the reaction center (i.e., there could be a weakening of the polarization of the C-C bond) due to the interaction of the solvating molecule and the  $-\text{CHCl}_2$  group. The decreased positive character of carbon would make the approach of water molecule more difficult. However, it would be difficult to say if there is any element of truth in the picture given above since the reaction center is next to the polar group involved. Strong solvation would result in the mutual polarization of both dipoles involved. The increased positivity of the  $\alpha$ - carbon would thus enhance inductive withdrawal of electrons from the reaction center. If this is actually what happens, and if the observed trend of  $k_{\text{termolecular}}$  with change of D is to be interpreted on the basis of alteration of the electrical character of the carboxyl carbon, then one has to postulate : replacement of water by acetone in the sphere of solvation of the  $-\text{CHCl}_2$  group.

It is hard to say whether the diversion of the lines of force of the dipole concerned or its enhanced polarization, when strongly solvated, is the predominant factor in determining the change in potential of the dipole system at the reaction center, without any

knowledge of the geometry of solvation.

It appears from the above discussion that the direct field effect of the negative chlorine atoms in  $\alpha$ -position affords the most reasonable explanation of the observed variations of reaction rate with dielectric constant.

The linear correlation between  $\log P_Z$  and  $\frac{1}{\sqrt{E}}$  which Fairclough and Hinshelwood (3) had observed in a large number of cases and which had been accounted for on the basis of some statistical considerations is found to hold good for the data presented here (Fig. 4).

References

1. Nair, P. M., and Anantkrishnan S. V., Proc. Ind. Acad. Sci. 32, 85, (1950).
2. Hockersmith, J. L., and Amis, E. S., Anal. Chem. Acta, 9, 101 (1953).
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